

***Perfluorinated Chemicals (PFCs) –
Emerging Drinking Water Contaminants
and
Occurrence in New Jersey Public Water Supplies***

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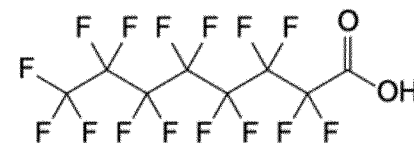
***National Water Monitoring Conference
Cincinnati, Ohio
April 30, 2014***



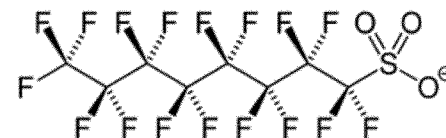
The conclusions expressed in this presentation do not necessarily reflect the policies of NJDEP.

What are PFCs?

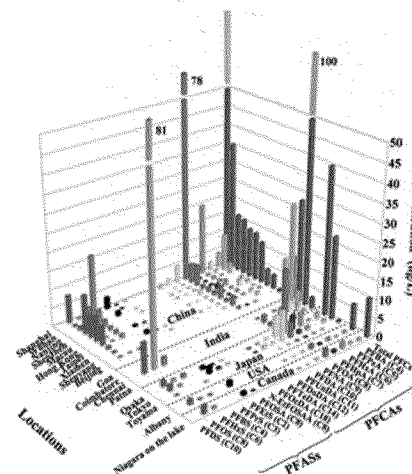
- Class of manmade chemicals.
 - Commercial and industrial uses.
 - Produced and used for over 60 years.
- Chemical Structure
 - Totally fluorinated carbon chain.
 - Length varies among compounds.
 - Charged functional group.
 - Carboxylates (COOH)
 - Sulfonates (SO₃⁻)
- Current focus is on broad suite of PFCs.
 - Perfluorooctanoic acid (PFOA, C8) & perfluorooctane sulfonate (PFOS) were main focus of early studies.
 - Mixtures of many PFCs are now known to be present in water, other environmental media, and human serum.



Perfluorooctanoic acid (PFOA)



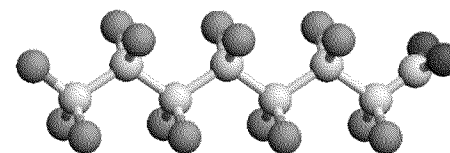
Perfluorooctanesulfonate (PFOS)



Mak et al. 2009. *Environ. Sci. Technol.* 43: 4824–29.

Important Properties of PFCs

- Repel oil and water.
 - Hydrophobic/oleophobic fluorinated carbon chain.
 - Useful for commercial and industrial applications.
- Highly water soluble.
 - Hydrophilic charged functional group.
 - *Occur in groundwater, surface water, and finished drinking water.*
- Chemically & thermally non-reactive.
 - Extremely strong C-F bond.
 - Useful for commercial and industrial applications.
 - *But do not break down in the environment.*

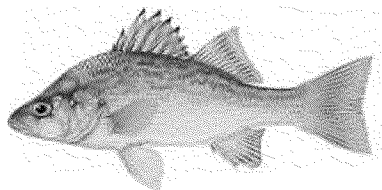


Environmental Fate & Transport of PFCs

- **Persistent, Bioaccumulative, and Toxic...**

- BUT very different from “classic” PBT chemicals

	PFCs	Dioxins & PCBs
Highly water soluble	YES	NO
Bind well to soil & sediments	NO	YES
Degrades in environment to some extent	NO	YES
Bioaccumulates in fish	NO/YES*	YES
Bioaccumulates in lipids	NO	YES
Drinking water is major exposure route	YES	NO



* **NO** - Less than 8 fluorinated carbons (e.g. *PFOA*, *PFHxS*).
YES – 8 or more fluorinated carbons (*PFOS*, *PFNA*, and higher).

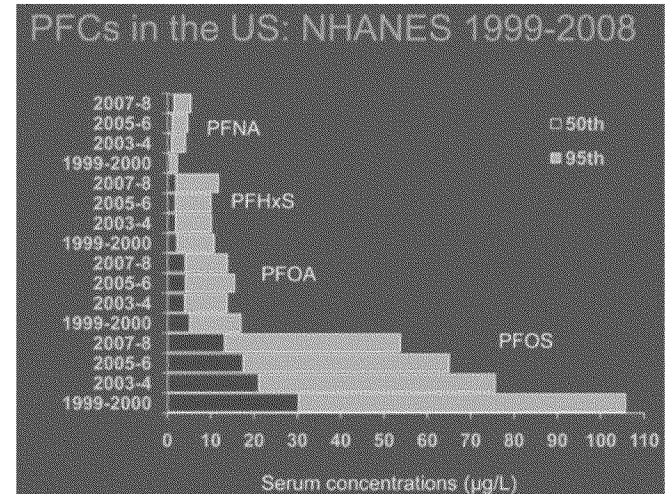
Some PFCs of Potential Concern in Drinking Water

PFOA – Perfluorooctanoic acid, C8

PFNA - Perfluorononanoic acid; C9

PFOS - Perfluorooctane sulfonate, C8-S

PFHxS - Perfluorohexane sulfonate, C6-S



Why are these four PFCs of potential concern?

Kato et al. Environ. Sci. Technol.
2011. 45: 8037-45

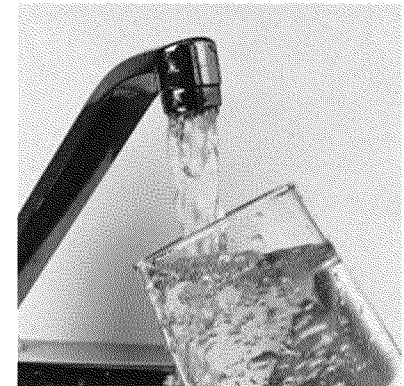
- Found ubiquitously in human blood serum..
- Biologically persistent - Human half-life is several years.
- More toxic than shorter chain PFCs.
- Relatively low drinking water concentrations substantially increase total exposure.
- U.S. production has stopped or is being phased out.
 - Replacements have been introduced.
- Included in USEPA nationwide drinking water monitoring program (UCMR3).

PFCs in Raw versus Finished Drinking Water

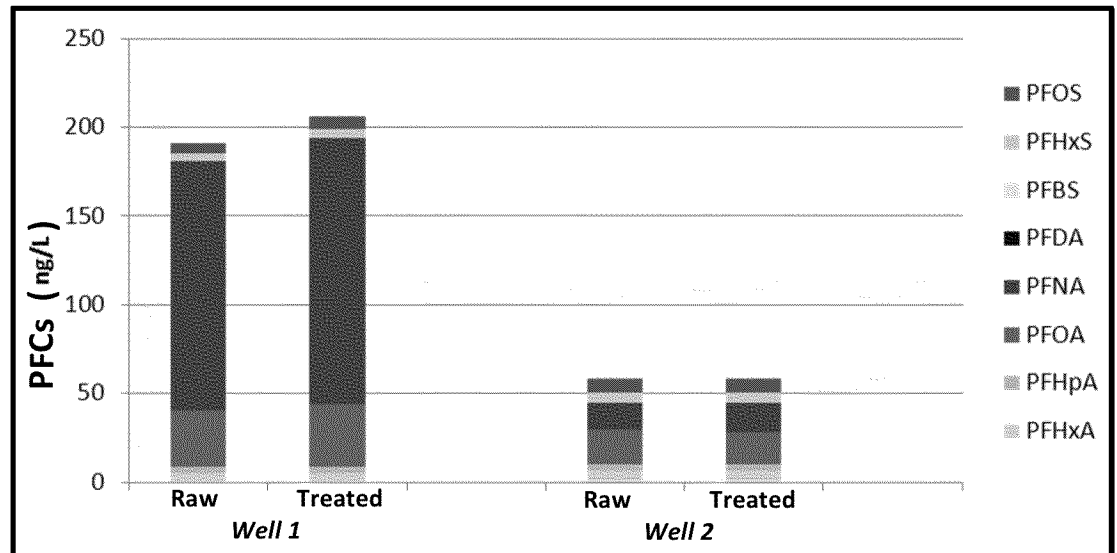
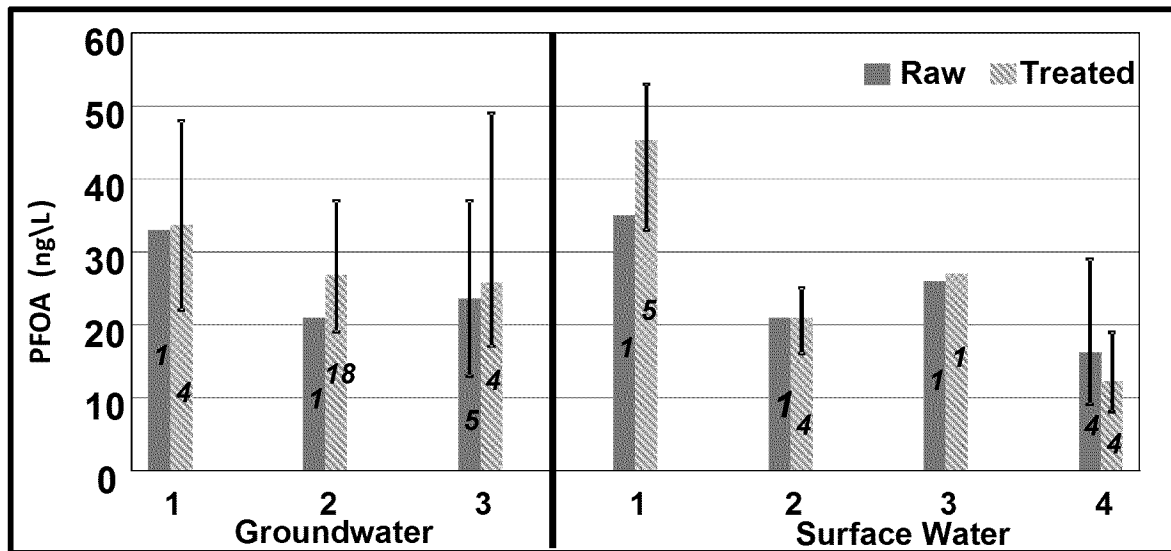
- Source water is generally a good indicator of finished water
 - Not removed by conventional drinking water treatment processes.



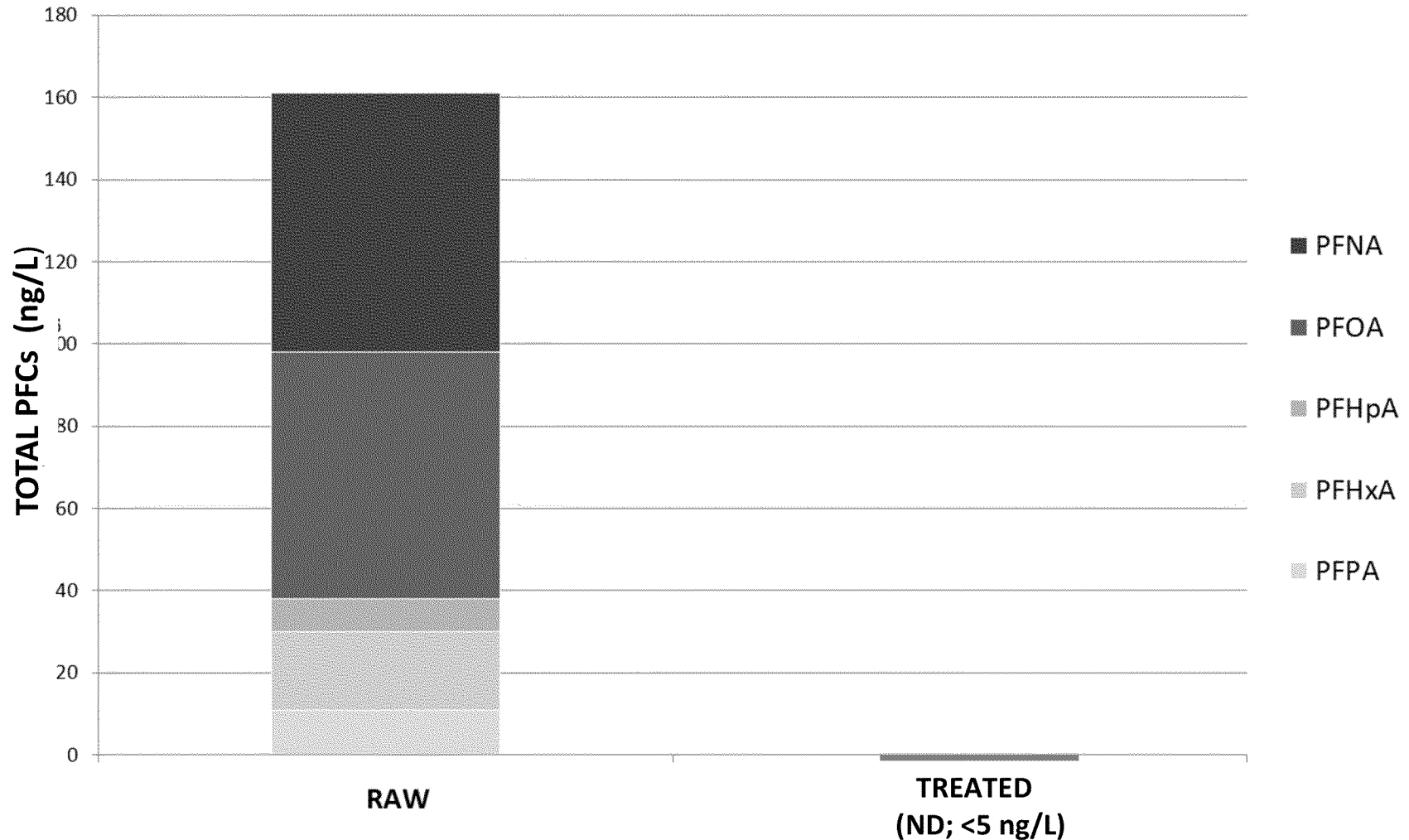
- Can be removed from drinking water by treatment systems specifically designed for PFC removal.
 - Granular activated carbon
 - Reverse osmosis.
 - Possibly ion exchange.



Raw versus Treated Water in NJ Public Water Systems Without Treatment Designed for PFC Removal

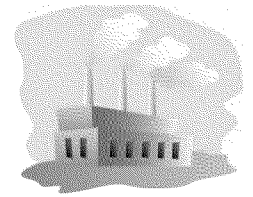


Raw versus Treated Groundwater at NJ Public Water System with Granular Activated Carbon Designed for PFC Removal



Sources of Environmental Contamination of PFCs

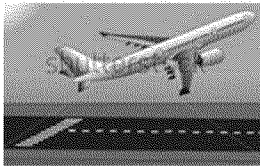
- Industrial facilities where made or used.
 - Processing aids in production of fluoropolymer plastics.
- Wastewater treatment plants.



- Effluent discharges.
- Land application of sludge.



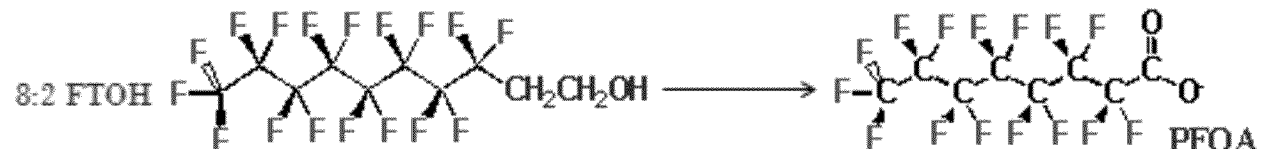
- Release of aqueous fire fighting foams.



- Firefighter training sites.
- Military bases & airports.



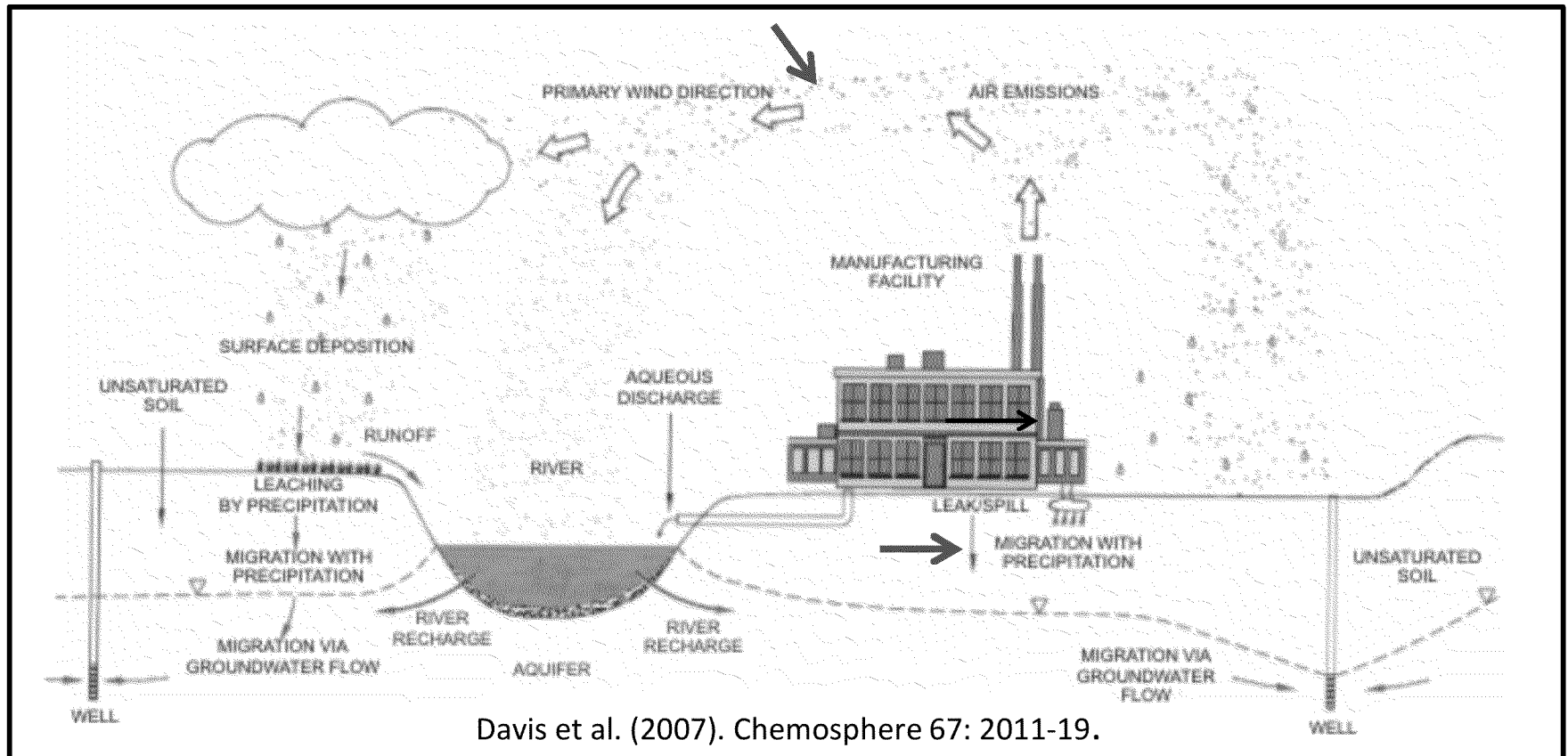
- Disposal of products used by small businesses.
 - Including chrome plating.
- Municipal landfill leachates.
- Formation from precursors in atmosphere, & by bacteria in soil, sludge, & wastewater.



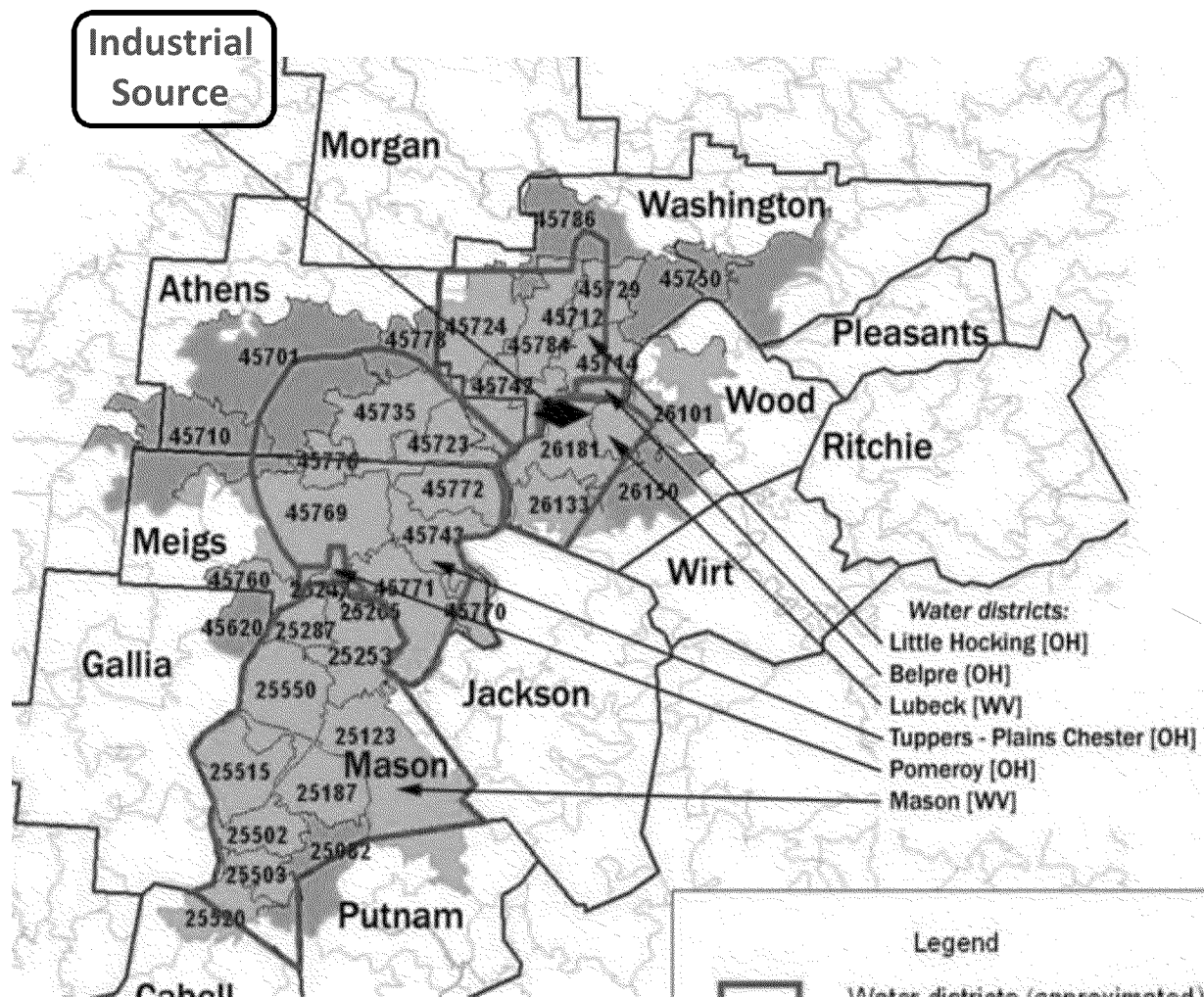
Transport of PFOA after Discharge from Fluoropolymer Production Facility

Two pathways for: Industrial releases —→ Groundwater:

1. Migration of groundwater plume
2. Air emissions —→ Soil deposition —→ Migration to groundwater



Drinking water wells up to ~20 miles from industrial source were contaminated with PFOA through air deposition (WV & Ohio).



Source: S. Frisbee,
 West Virginia Univ.
 School of Medicine. 2008.



PFCs in Drinking Water Wells Near NJ Industrial Sites

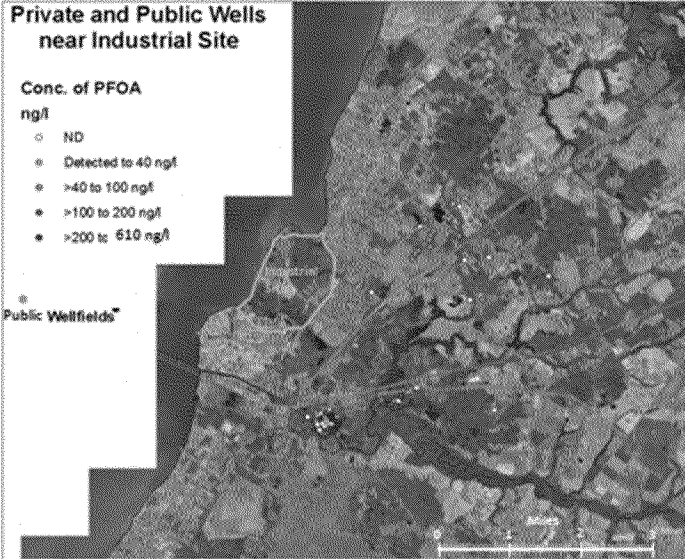
PFOA– Salem County, NJ

Private and Public Wells
near Industrial Site

Conc. of PFOA
ng/l

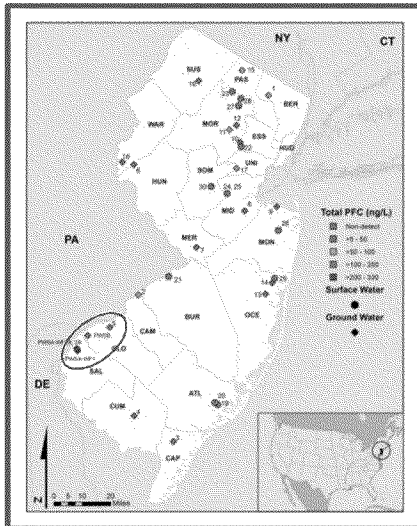
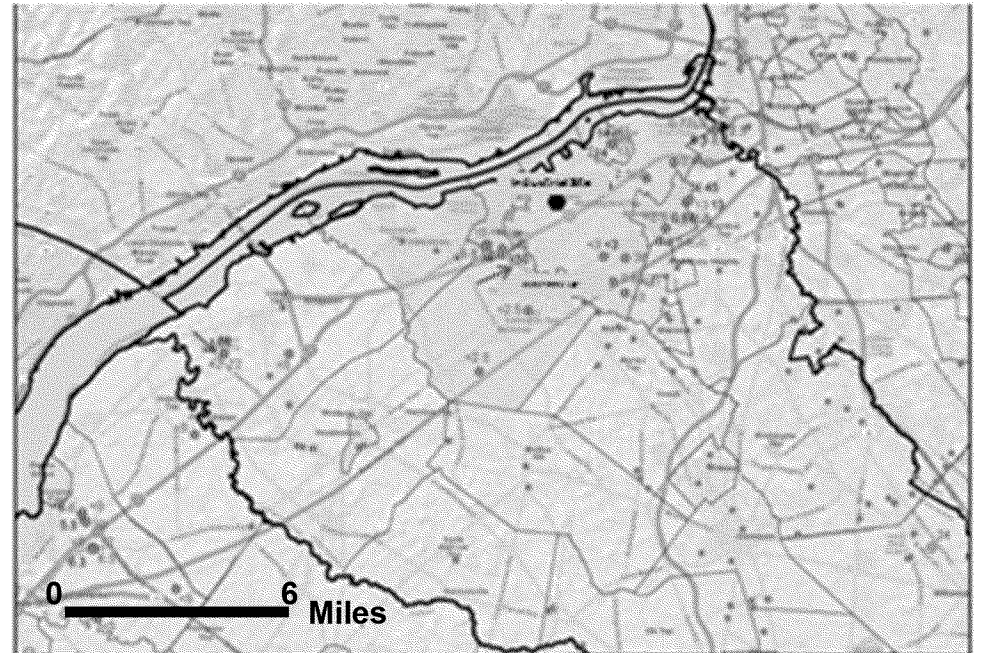
- ND
- Detected to 40 ng/l
- >40 to 100 ng/l
- >100 to 200 ng/l
- >200 to 610 ng/l

Public Wellfields*



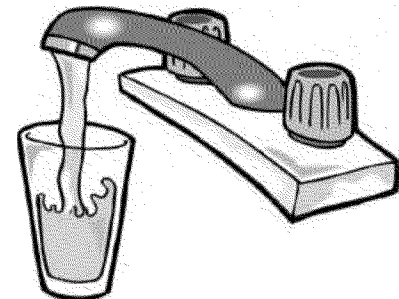
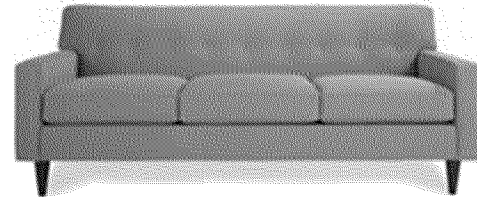
*Detected in public water supply wells at up to 280 ng/L.

Perfluorononanoic acid (PFNA,C9) in Public Water System Wells in Gloucester County, NJ



Sources of General Population Exposure to PFCs

- PFCs are present in blood serum of the general populations at ppb ($\mu\text{g/L}$) levels.
- Total Exposure = PFCs + Metabolism of precursors to PFCs.
- Diet:
 - Food + food packaging.
- Consumer products including:
 - Stain resistant carpets, upholstery.
 - Waterproof/breathable clothing.
 - Protective sprays, ski waxes etc.
 - *Non-stick cookware not considered to be major source.*
- Indoor & outdoor air, house dust.
- **Drinking Water**
 - *% of total exposure is highly dependent on drinking water concentration.*



Relatively Low Drinking Water Concentrations Substantially Increase Total Human Exposure to PFOA

- With ongoing exposure to PFOA, blood serum levels ↑ by at least 100-fold the drinking water concentration, on average.
- Similar or higher ratio for other biologically persistent PFCs (e.g. PFNA, PFOS, PFHxS).
- Ratio is higher in children, on average.

<i>Drinking Water Concentration (ug/L)</i>	<i>Increase in Serum Conc. (ug/L)</i>	<i>% Increase in Serum Level *</i>	<i>% Total Exposure From DW*</i>
0.001	0.1	2.5%	2.4%
0.01	1	25%	20%
0.04 **	4	100%	50%
0.1	10	250%	71%
0.4	40	1000%	91%

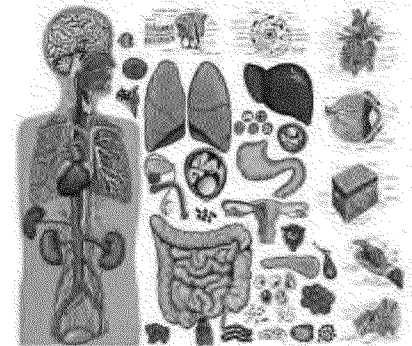
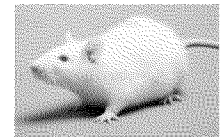
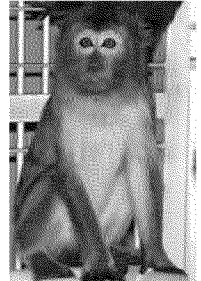
Post et al. (2012)

** Assuming 4 ug/L background serum level (U.S. median).*

*** Current New Jersey Health-based Guidance.*

Health Effects Summary

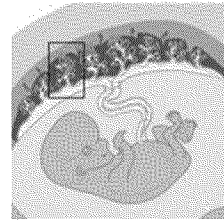
- Similarities and differences in effects among PFCs.
 - Longer chain PFCs generally more toxic & biologically persistent.
- Animal toxicology
 - Includes liver, immune system, developmental, endocrine, metabolic, and neurobehavioral toxicity.
 - PFOA and PFOS caused tumors in chronic rat studies.
 - Other PFCs not tested.
- Human health effects associated with PFC(s) in the general population and/or communities with contaminated drinking water include:
 - ↑ cholesterol
 - ↑ uric acid
 - ↑ liver enzymes
 - ↓ birth weight
 - ↓ vaccine response
 - Thyroid disease
 - Osteoarthritis
 - Diabetes
 - Testicular and kidney cancer
 - Pregnancy-induced hypertension
 - Ulcerative colitis
 - Effects in young adulthood from prenatal exposures
 - *Obesity in young women.*
 - *↓ sperm count in young men.*



Developmental Exposures to PFCs are Important

- Developmental effects are sensitive endpoints of toxicity.

- Prenatal exposure to fetus.



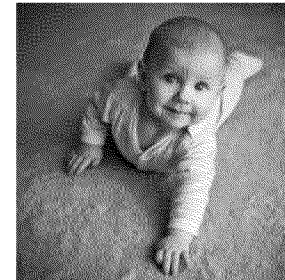
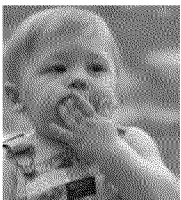
- Infants consume much more fluid on body weight basis.



- PFCs are present in breast milk
- Formula prepared with contaminated drinking water.

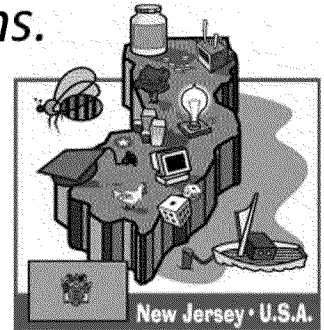


- Hand-to-mouth behavior: House dust.
- More time on floors: Treated carpets.



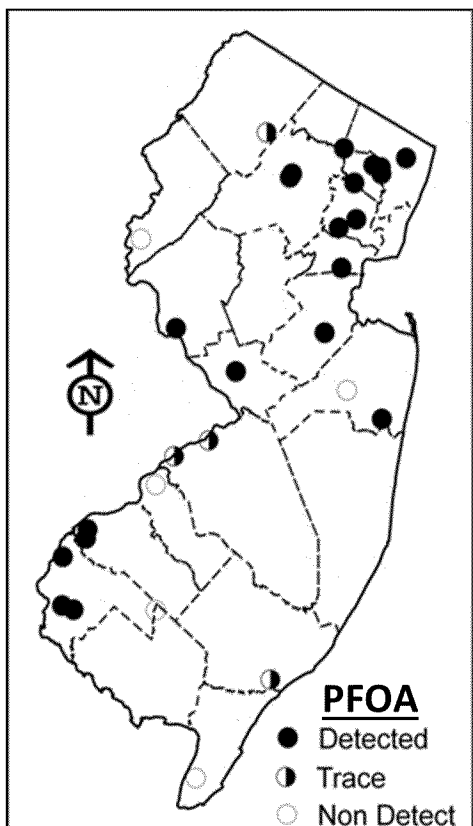
Summary of NJ Public Water System PFC Occurrence Data

- First state to conduct statewide PFC occurrence studies.
 - *Two NJDEP studies (2006 and 2009-10).*
 - *Additional data submitted by public water systems and others.*
- NJDEP Office of Science PFC database (2006 - present):
 - *190 sampling locations from 69 public water systems.*
 - *627 samples (269 raw & 358 finished water).*
 - *374 (60%) : PFOA & PFOS only.*
 - *253 (40%) : Broader suite of PFCs.*
- USEPA Unregulated Contaminated Monitoring Rule (UCMR3).
- PFOA detected above NJ guidance (40 ng/L) in at least one finished water sample from 8 public water systems.



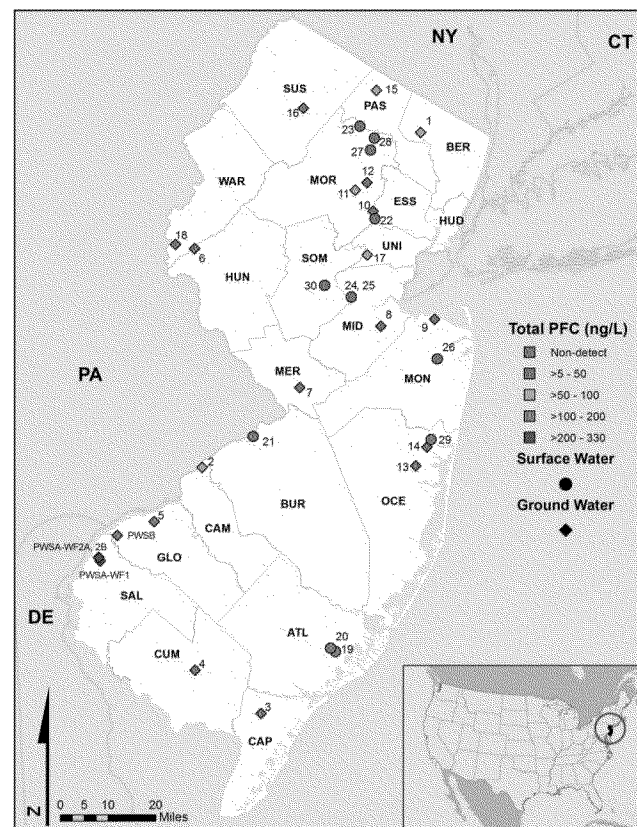
Public Water Systems (PWS) Sampled in NJDEP Studies

2006 Study (23 PWS - PFOA & PFOS)



PFOA – 65%; PFOS - 30%
(≥ 4 ng/L).

2009-2010 Study (31 PWS - 10 PFCs)

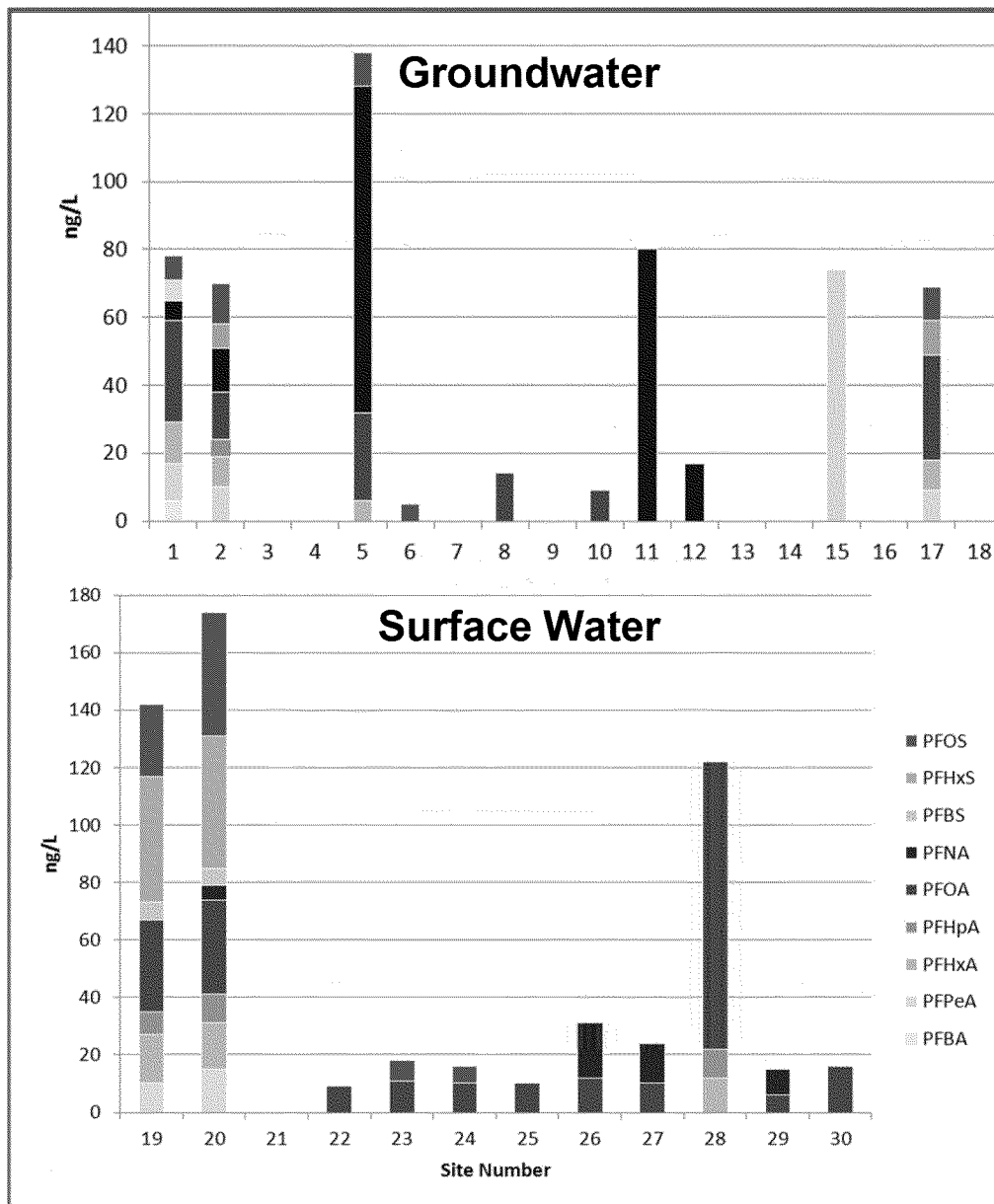


2009-10 NJDEP Study of 10 PFCs in Public Water Systems

- Raw water from 31 public water systems in 20 of 21 NJ counties.
- PFCs analyzed:
 - Seven carboxylates (C4-C10):
 - *Perfluorobutanoic acid (PFBA, C4)*
 - *Perfluoropentanoic acid (PFPeA, C5)*
 - *Perfluorohexanoic acid (PFHxA, C6)*
 - *Perfluoroheptanoic acid (PFHpA, C7)*
 - *Perfluorooctanoic acid (PFOA, C8)*
 - *Perfluorononanoic acid (PFNA, C9)*
 - *Perfluorodecanoic acid (PFDA, C10)*
 - Three sulfonates (C4-S, C6-S, C8-S)
 - *Perfluorobutane sulfonate (PFBS, C4-S)*
 - *Perfluorohexane sulfonate (PFHxS, C6-S)*
 - *Perfluorooctane sulfonate (PFOS, C8-S)*



Results of 2009-10 NJDEP Study of 10 PFCs in NJ PWS



- Between **1 and 8 PFCs** in 70% of PWS.
 - **ND** in 30% of PWS (≤ 5 ng/L).
- **Total PFCs:** 9-174 ng/L.
- **PFOA:** Most frequently detected (57%); up to 100 ng/L.
 - But other PFCs found at some sites where PFOA not detected.
- **PFOS:** 30%; up to 43 ng/L.
- **PFDA (C10):** Not detected.
- **Other PFCs:** 3% to 23% of PWS.
- **PFNA (C9):** Up to 96 ng/L; higher than reported elsewhere.
- No apparent relationship of PFCs with developed land use.
- Possible sources identified at some sites; unknown at others.
- PFOA and PFOS results similar to 2006 NJDEP study.

USEPA Unregulated Contaminated Monitoring Rule (UCMR3)



- Required monitoring of finished water from U.S. PWS
 - Sampling in 2013-15.
 - All large (>10,000 customers) and a few small PWS.
 - 6 PFCs, as well as other unregulated contaminants.
- Much higher Reporting Levels than for other NJ PFC drinking water data from certified laboratories.
- Initial UCMR3 data (45% of large NJ PWS):
 - PFOA & PFNA found more frequently in finished water from NJ public water systems than nationally.

Initial Unregulated Contaminant Monitoring Rule 3 Data: New Jersey versus National PFC Finished Water Detections

<i>Compound</i>	<i>Reporting Level (ng/L)</i>	<i>NJ PWS (# Detects)*</i>	<i>NJ PWS (% Detects)</i>	<i>National PWS (# Detects Other than NJ)**</i>	<i>National PWS (% Detects Other Than NJ)</i>
PFOA (C8)	20	7/75	9.3%	19/1405	1.4%
PFNA (C9)	20	2/75	2.7%	2/1405	0.1%
PFOS (C8-S)	40	1/75	1.5%	23/1405	1.6%
PFHxS (C6-S)	30	0/75	0%	14/1405	1%
PFBS (C4-S)	90	0/75	0%	1/1405	0.07%
PFHpA (C7)	10	1/75	1.5%	16/1405	1.1%
Any PFC	-----	11/75	14.7%	<75/1405***	<5.3%***

* New Jersey data as of 4/9/14.

** USEPA data posted online as of 2/14.

*** Actual National # and % detections for “Any PFC” are substantially lower than shown due to detections of multiple PFCs in many PWS.

Conclusions

- PFCs occur in surface water, groundwater, and finished drinking water.
 - *Source water generally good indicator of finished drinking water.*
 - *But can be removed by specifically designed treatment systems.*
- PFOA and PFNA appear to occur more frequently in New Jersey public water systems than nationally, based on initial UCMR3 data.
- Drinking water can be an important human exposure route for PFCs.
- Human and animal data suggest potential health risks from PFCs in drinking water.
- Infants are a susceptible sub-population for PFCs in drinking water.
 - *Developmental effects are sensitive endpoints of toxicity.*
 - *Exposures are higher than in adults using same drinking water source.*
- Future work is needed to assess the risks of individual PFCs and mixtures of PFCs found in drinking water.

Publications

- Post, G.B., Louis, J.B., Cooper, K.R., Boros-Russo, B.J., Lippincott, R.L. (2009). Occurrence and potential significance of perfluorooctanoic acid (PFOA) detected in New Jersey public drinking water systems. *Environ. Sci. Technol.* 43, 4547–4554.
- Post, G.B., Cohn, P.D., and Cooper, K.R. (2012). Perfluorooctanoic acid (PFOA), an emerging drinking water contaminant: a critical review of recent literature. *Env. Res.* 116, 93-117.
- Post, G.B., Louis, J.B., Lippincott, R.L., and Procopio, N.A. (2013). Occurrence of perfluorinated chemicals in raw water from New Jersey public drinking water systems. *Environ. Sci. Technol.* 47, 13266-75.
- New Jersey Dept. of Environmental Protection (2014). Draft Technical Support Document: Interim Specific Ground Water Criterion for Perfluorononanoic Acid (PFNA, C9). March 21, 2014.

Acknowledgements

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Thank you!

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Additional Topics

- Current Regulatory Status & Existing Drinking Water Guidelines
- Worldwide Environmental Occurrence & Transport
- Phase-out & Replacements for Long Chain PFCs
- Human Epidemiology Studies of PFOA/PFCs
- Developmental Exposures and Effects
- Health Effects of Perfluorinated Sulfonates and PFNA

Current Regulatory Status & Existing Drinking Water Guidelines

Current Regulatory Status

- No USEPA or New Jersey enforceable drinking water standards.
- PFOA and PFOS listed on **USEPA Contaminant Candidate List 3** for consideration for future regulation.
 - **IF** positive **Regulatory Determination**, timeframe for proposal of MCL is at least several years after UCMR3 study is completed.
- **New Jersey Drinking Water Quality Institute**
 - Charged with developing recommendations for drinking water standards (MCLs) to NJDEP.
 - Will evaluate PFNA, PFOA, & PFOS.



Drinking Water Guidance & Draft Groundwater Criterion

PFOA

- *NJDEP Health-based Drinking Water Guidance (2007): 40 ng/L.*
 - Based on **chronic** (lifetime) exposure
 - Recent epidemiology and toxicology data not considered.
- *USEPA Provisional Health Advisory (2009): 400 ng/L.*
 - Based on **short-term** exposure.

PFOS

- *USEPA Provisional Health Advisory (2009): 200 ng/L.*
 - Based on **short-term** exposure.

PFNA

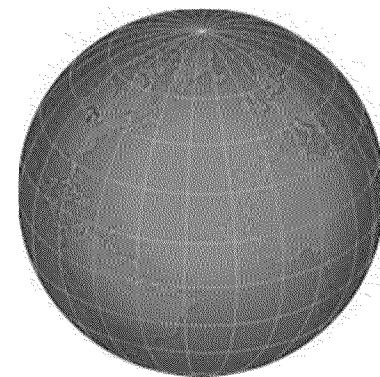
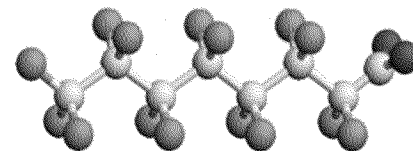
- *Draft NJDEP Interim Groundwater Criterion: 20 ng/L.*
- Has not been evaluated by USEPA or other states.
 - Based on **chronic** (lifetime) drinking water exposure
 - Public comment period ends May 1, 1014.

Worldwide Environmental Occurrence & Transport

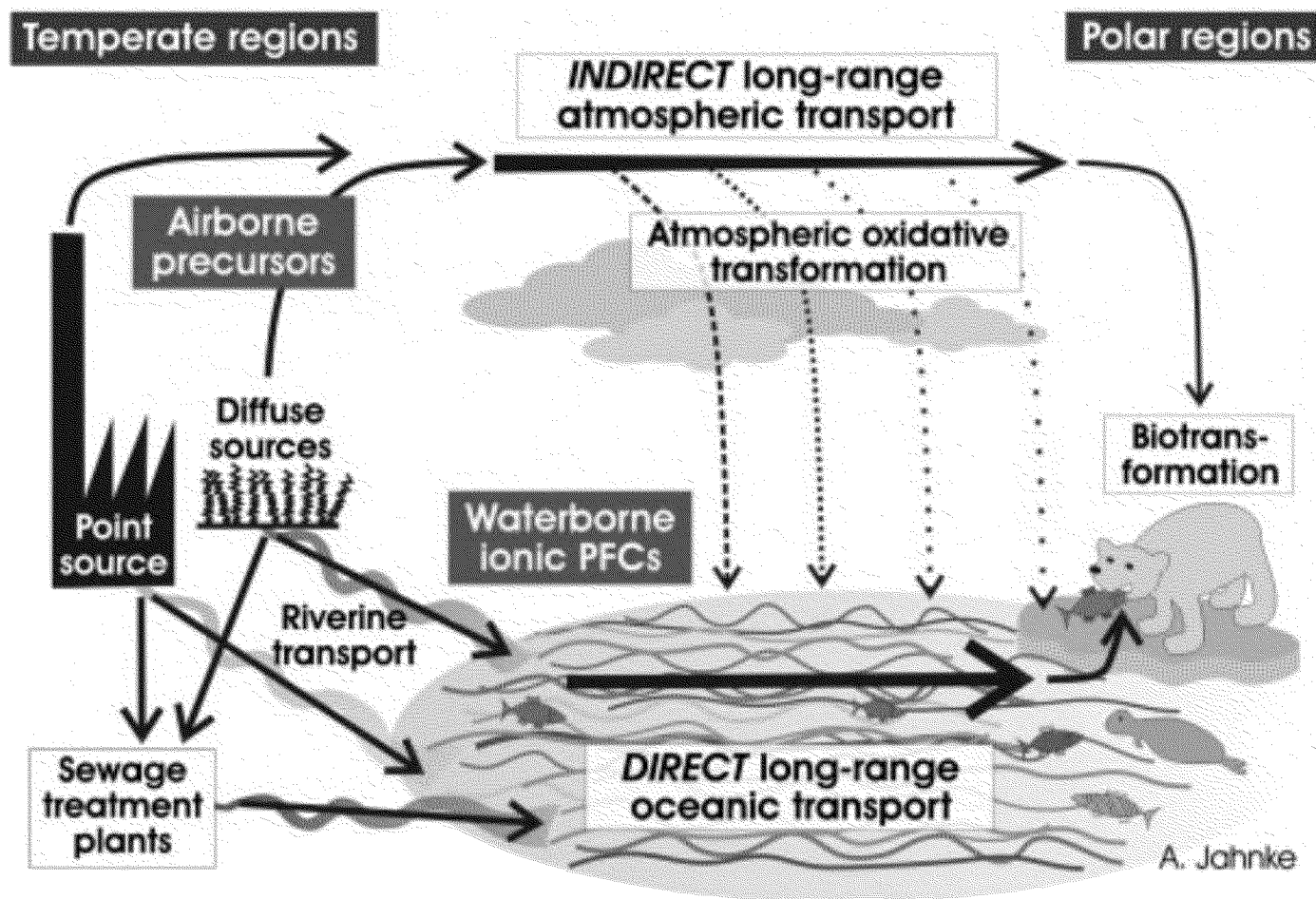
PFCs Found in Environmental Media Worldwide

Found in many environmental media including...

- Ground water & surface water
- Drinking water (public supplies & private wells)
- Air (indoor & outdoor)
- Sludge (“biosolids”) from WWTP (sewage treatment plants)
- Soil
- Sediments
- Dust (outdoor & indoor)
- Plants, including food crops
- Wildlife, including in **remote regions** (Arctic)
- Polar ice caps



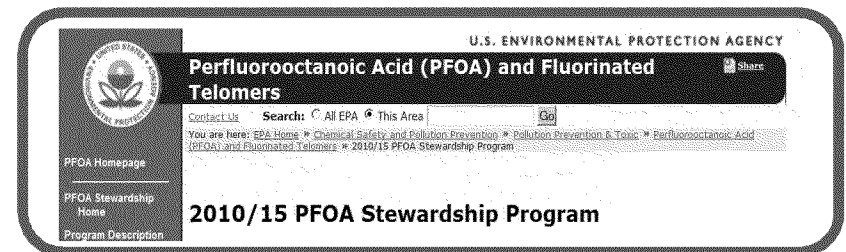
Long Range Transport Pathways for PFCs



Phase-out & Replacements for Long Chain PFCs

Production of PFCs

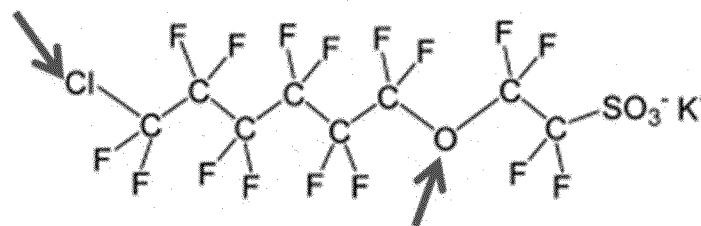
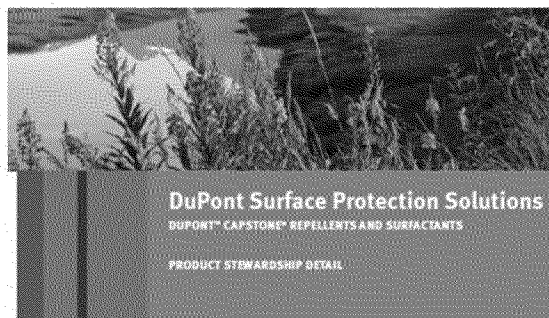
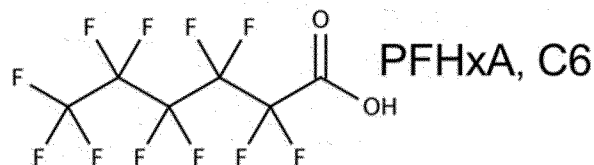
- Produced for decades (*PFOA, >60 years; PFOS, >50 years*)
- **PFOA, PFNA, PFOS, PFHxS, and other long chain homologues** – Production by major U.S. manufacturers has been/is being voluntarily ended.
- **Environmental contamination expected to continue due to:**
 - Extreme environmental persistence.
 - Continued formation from precursors.
 - Continued production by non-participating manufacturers, especially overseas.
- *Shorter chain PFCs and other types of polyfluorinated compounds introduced as replacements.*



Replacements for Phased-out PFCs (e.g. PFOA, PFNA, PFOS, PFHxS)

- Shorter chain PFCs or other types of *polyfluorinated* compounds.
- Generally less biologically persistent & less toxic but...
 - May need to be used in greater amounts.
 - Toxicity information is often limited.
- Like other PFCs, do not degrade in environment.
- Some are not detected by standard analytical methods.
 - Research analytical methods needed.

Examples of Replacements for Phased-out PFCs

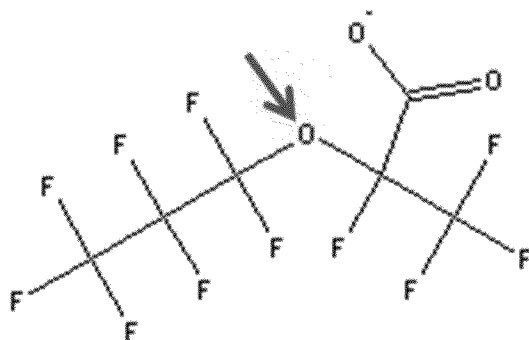


Environmental
Science & Technology

Article
pubs.acs.org/est

First Report of a Chinese PFOS Alternative Overlooked for 30 Years: Its Toxicity, Persistence, and Presence in the Environment

Siwen Wang,[†] Jun Huang,^{*†} Yang Yang,[†] Yamei Hui,[†] Yuxi Ge,[†] Thorjörn Larssen,[‡] Gang Yu,[†] Shubo Deng,[†] Bin Wang,[†] and Christopher Harman[‡]



Undecafluoro-2-methyl-3-oxahexanoic acid

“Potential Immunotoxicity of a Polyfluoroalkyl Substance Replacement of Perfluorooctanoic Acid”
Jamie DeWitt, Blake R Rushing, Qing Hu, East Carolina Univ. Mark Strynar, US EPA, RTP, North Carolina

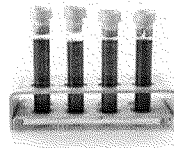


Human Epidemiology Studies for PFOA/PFCs

Human Epidemiology for PFCs

- **Advantage:** Human data are most relevant to human risk.
- **Caveats:**
 - Not a “controlled” experiment.
 - Associations: “*Causality not proven*” – due to nature of the studies.

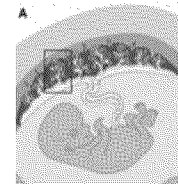
- **Internal doses** (serum levels) reduce uncertainty about exposure.



- **Three types** of populations :
 - Workers (highly exposed).
 - Communities with contaminated drinking water.
 - General population (NHANES & other).



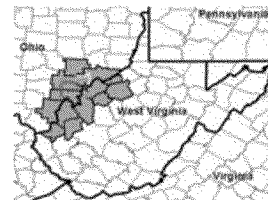
- **Timing of exposures** may be important.
 - Developmental exposures → effects later in life.
 - Most studies not designed to evaluate this.



- **Overall conclusions** based on total body of evidence (positive and negative)



Studies of WV/Ohio Communities with PFOA-Contaminated Drinking Water -“C8 Health Study”



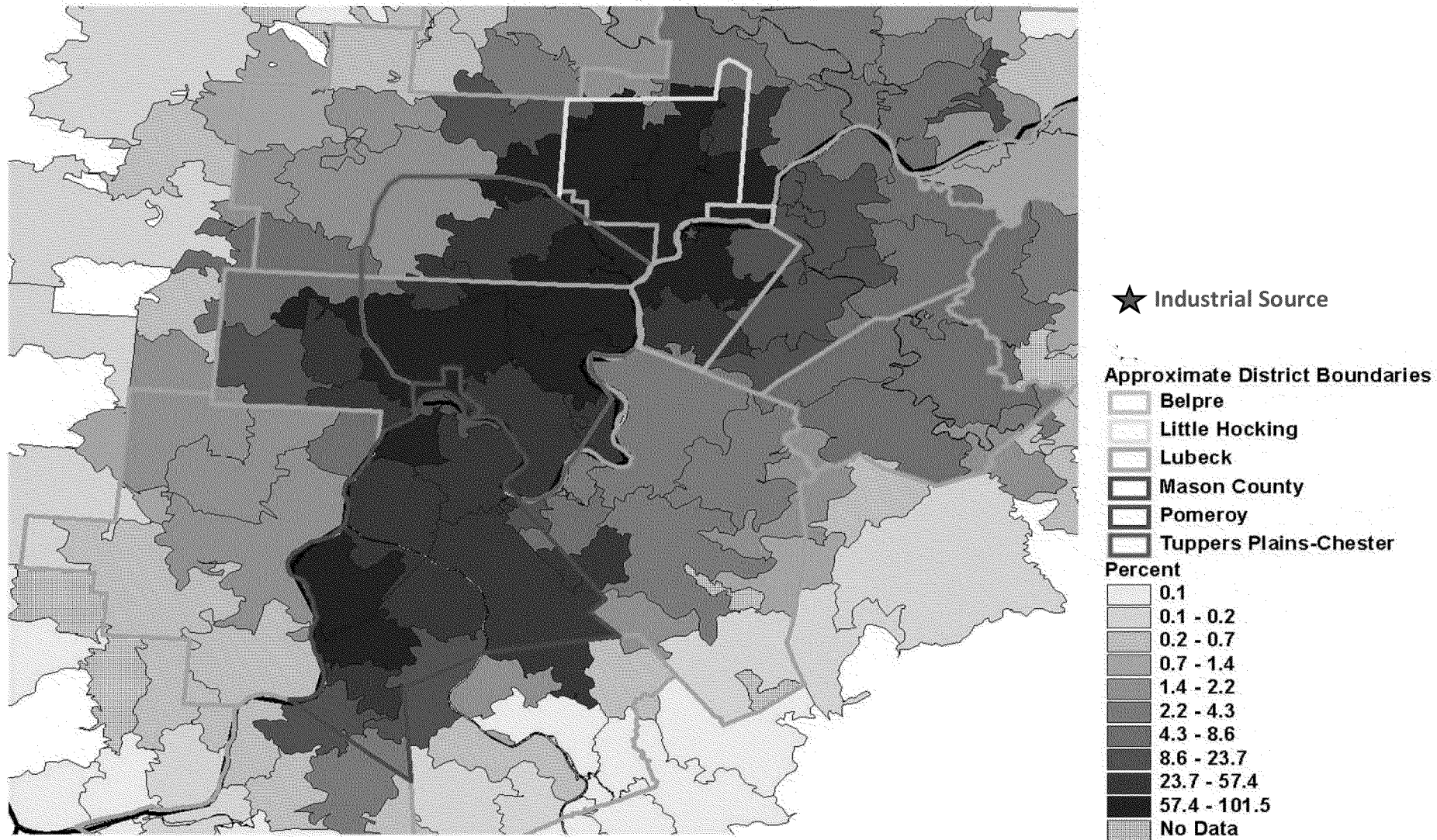
- Unique study with many components and researchers:
 - Huge size: *~70,000 subjects* (infants to very elderly).
- 6 water districts impacted by fluoropolymer manufacturing emissions for ~50 yrs.
 - Drinking water levels: $\geq 0.05 \text{ ug/L}$ (*50 ng/L*) to over 3 ug/L (*3000 ng/L*)
 - Includes *public water supply & private well* users.
- *C8 Science Panel* determined if ***probable links*** between diseases & exposure:
 - Defined as: “... *given the scientific evidence available, it is more likely than not that a connection exists between C8 exposure and a particular human disease among class members....*”
 - Funded as part of 2004 settlement of class action lawsuit.



C8 Science Panel

[Home](#)

Percent of C8 Study Participants in Relation to Total 2000 Census Population For ZIP Code Tabulation Areas (ZCTAs)



Source: S. Frisbee,
West Virginia Univ.
School of Medicine. 2008.



Effects Associated with PFOA Exposure in C8 Health Study

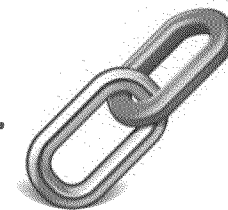


C8 Science Panel

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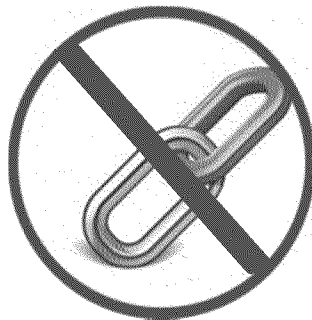
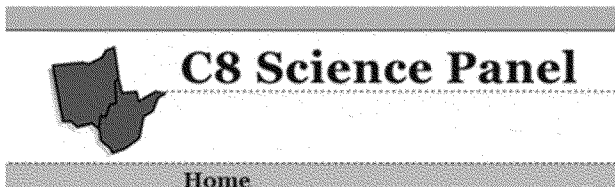
- Testicular cancer*
- Kidney cancer*
- Clinically elevated cholesterol in adults & children*
- Thyroid disease* & changes in *thyroid hormone levels*.
- Pregnancy-induced hypertension*
- Ulcerative colitis*
- Delayed puberty (girls)
- Osteoarthritis
- Clinically elevated uric acid (heart disease risk factor)
- ↑ liver enzyme in serum (marker of liver disease)
- Changes in markers of immune & inflammatory response

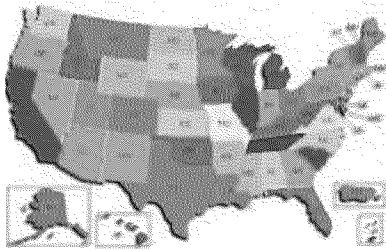
**C8 Science Panel conclusion of “Probable Link”.*



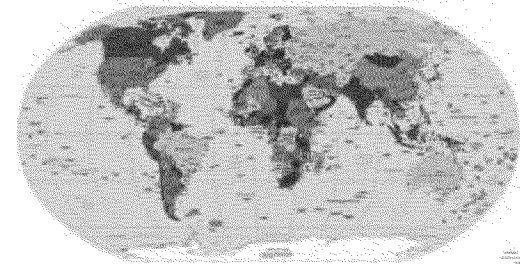
C8 Science Panel Conclusion of “No Probable Link” for:

- Cancers other than testicular & kidney cancer
- Rheumatoid arthritis & other autoimmune diseases
- Common infections (cold & flu)
- ADHD & Learning disabilities
- Asthma
- Stroke
- Diabetes (Types 1 & 2)
- Birth defects
- Miscarriage & Stillbirth
- Premature birth & Low Birth Weight
- Liver disease
- Kidney disease
- Osteoarthritis
- Parkinson’s disease
- Heart disease
- High blood pressure





General Population Studies

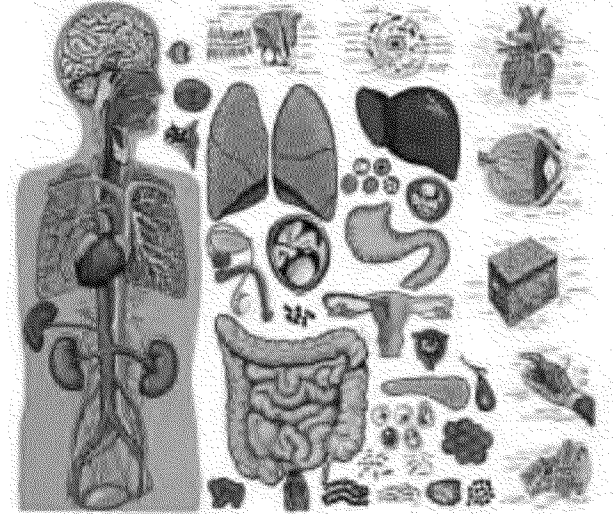


- From U.S. (NHANES) & other countries.
- Associations with numerous effects.
 - Many are consistent with worker studies and/or C8 Health Study.
- Relevant to **low-level exposures** from drinking water & other sources.
- *Do not have such data for most other drinking water contaminants.*



Health Effects Associated with PFOA in General Population

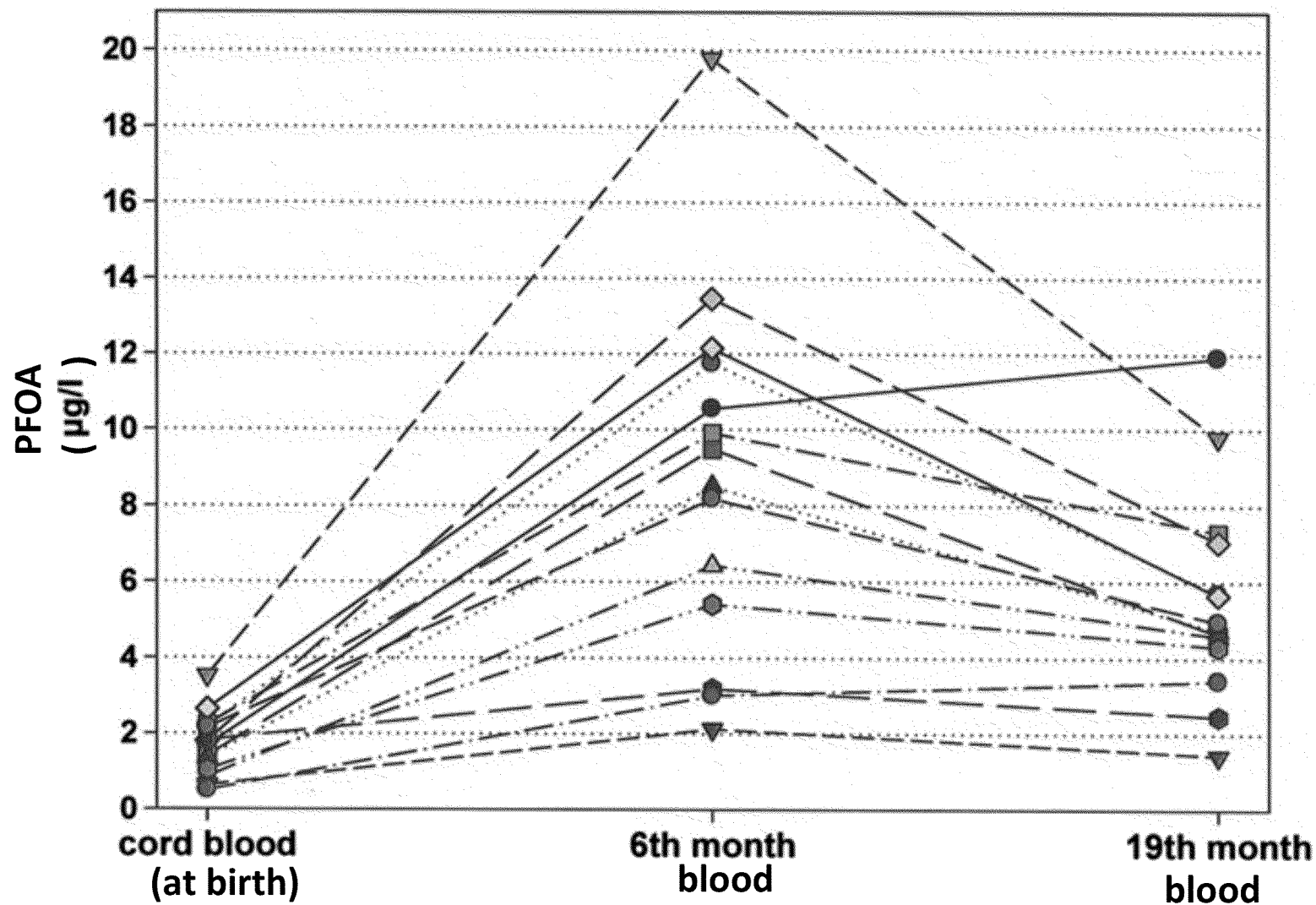
- Heart disease
- Thyroid disease
- ↑ cholesterol
- ↑ uric acid (children & adults)
- ↑ serum liver enzymes
- ↓ kidney function
- ↓ fetal growth (birth weight & other measures)
- ↓ vaccine response in children (in 2 study populations)
- ↑ sperm abnormalities
- ↓ fertility (increased time-to-pregnancy)
- ↑ osteoarthritis (women)
- ↑ asthma and IgE (children)



- Prenatal exposure associated with ***effects in adulthood:***
 - Obesity in young women
 - Decreased sperm count in young men
- ***Cancer incidence has not been adequately evaluated.***

Developmental Exposures & Effects

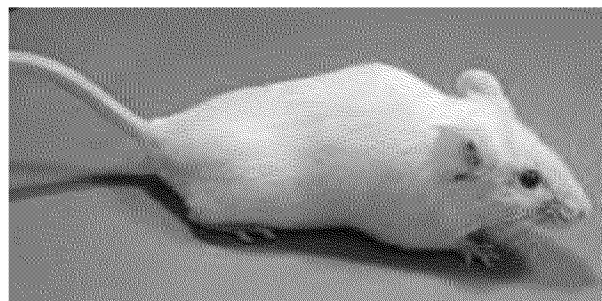
Infant Exposures to PFOA Increase During Breast-Feeding & Decrease at Weaning



Fromme et al. 2010. Env. Sci. & Technol. 44; 7123-29.

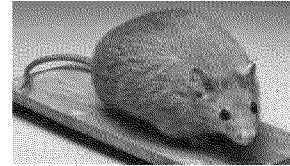
PFOA Developmental Effects in Mice

- Developmental exposures:
 - To **fetus** (through dosing of mother) *and/or*
 - To **pups** (through breast milk).
- Full litter resorptions
- ↓ pup survival & growth
- Delayed developmental milestones
- Sexual maturation
 - Delay – females
 - Acceleration – males
- Neurobehavioral effects in adulthood
 - From single dose to pups.
- Additional ***low dose*** effects....

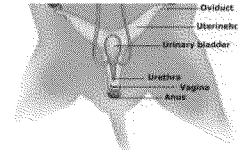


PFOA Low-dose Developmental Effects in Mice

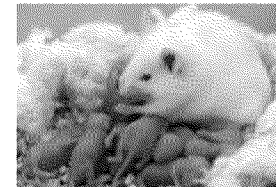
- At **lower doses** than other effects – no threshold identified.
- **Female Obesity** & hormone changes in early adulthood.
 - Consistent with recent human data.



- **Female reproductive tract structural abnormalities**



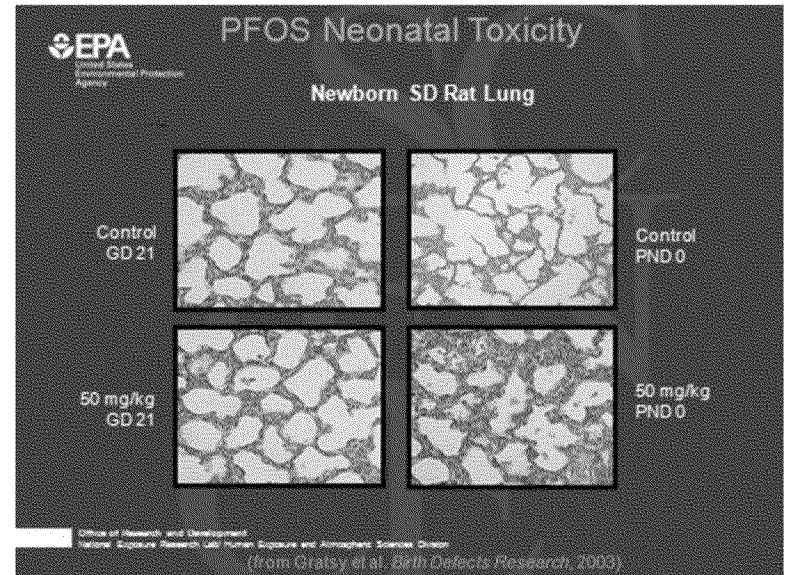
- **Delayed mammary gland development.**
 - From very short exposures to pups & pregnant/nursing dams.
 - Pup effects persist into adulthood.
 - Most sensitive known endpoint.
 - Effects from drinking water exposures relevant to human environmental exposures.
- ***For most other drinking water contaminants, toxicity in animals only at doses much higher than human exposure levels.***



Health Effects of Sulfonates & PFNA

Health Effects of Sulfonates

- Similarities and differences with PFOA
 - Mode of action
 - Toxicological effects.
- **PFOS:**
 - Extensively studied humans and animals
- **PFHxS :**
 - Longest known human half-life - 8.5 years.
 - But very little toxicology data.



Health Effects of PFNA (C9)

- Recent focus on Gloucester County drinking water contamination.
- Considerable database for comparison with PFOA.
- Available information suggests:
 - Similar profile of animal toxicity and human epidemiology as PFOA.
 - Same mode of action as PFOA.
 - More biologically persistent than PFOA.
 - More toxicologically potent than PFOA.
 - Same *in vivo* effects at lower (or much lower) doses.
 - More potent in *in vitro* receptor activation assays.

